CHENOPODIUM OIL. PART II.
THE HYDROCARBON FRACTION

BY

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CCXIX.—*Chenopodium Oil. Part II. The Hydrocarbon Fraction.*

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The presence of a lævorotatory component in the hydrocarbon fraction of chenopodium oil was first recognised by Kremers (*Pharm. Rev.*, 1907, **25**, 155), and since then numerous efforts have been made to isolate and identify it. Nelson obtained, by bromination of the hydrocarbon fraction, a substance which he regarded as *l*-limonene tetrabromide (*J. Amer. Chem. Soc.*, 1920, **42**, 1204), but on repeating this work the authors found that the product so obtained was optically inactive, differed in crystalline form and physical constants from all the known terpene tetrabromides, and therefore could not be *l*-limonene tetrabromide, but must be derived from a terpene so far unknown. Up to that time only *p*-cymene and α-terpinene had been definitely recognised as present (*J.*, 1921, **119**, 1714).

The authors now show that Nelson's tetrabromide (I) on treatment with silver acetate yields an acetoxybromide (II), which is oxidised by chromic acid to *p*-tolyl methyl ketone (IV), probably through the dihydroketone (III). These reactions are best explained
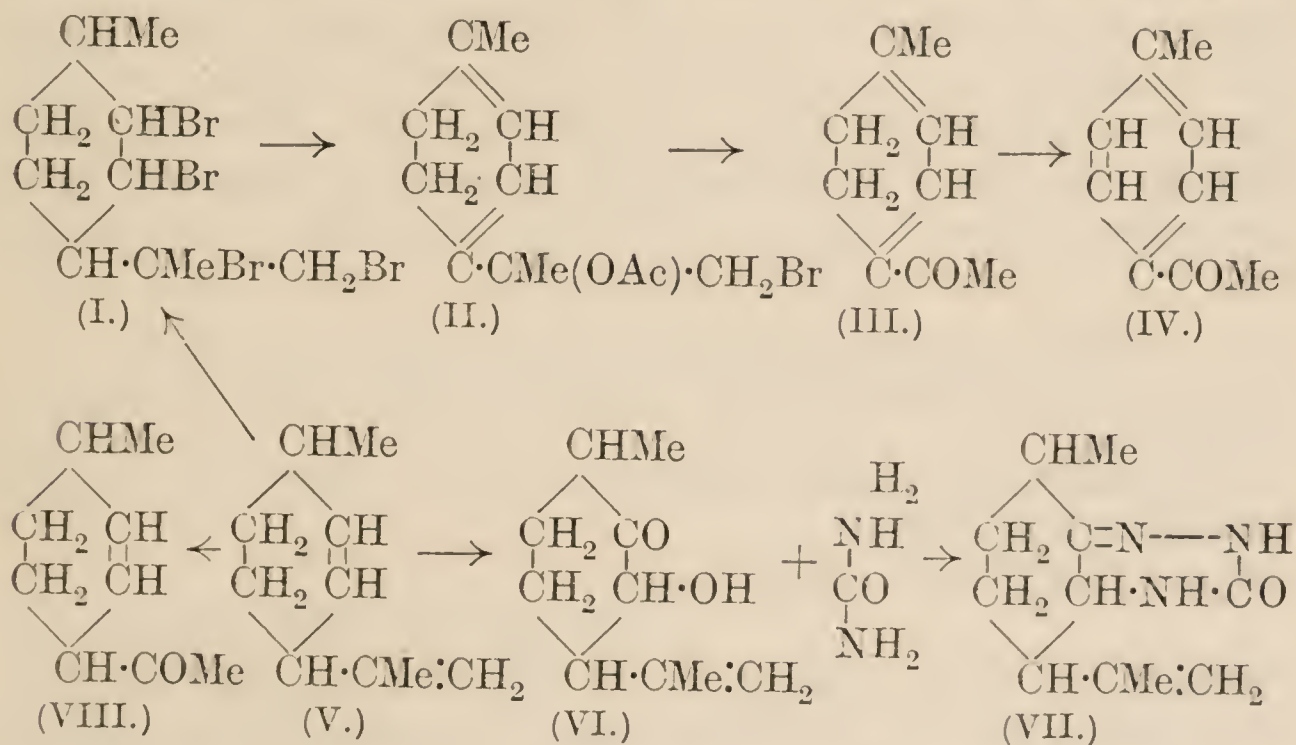
by the assumption that the tetrabromide is derived from the terpene $\Delta^{2,8,9}$-*p*-menthadiene (V). Support for this view is obtained from the fact that the total hydrocarbon fraction on treatment with chromic acid is partly oxidised to dimethyl-acetonylacetone (derived from α-terpinene) and a hydroxy-ketone, $C_{10}H_{16}O_2$ (VI), the semicarbazone of which readily loses water, like other *o*-hydroxy-ketones derived from hydroaromatic substances

(compare Manasse, *Ber.*, 1897, **30**, 668), forming a base, $C_{11}H_{17}ON_3$ (VII). Further, the total hydrocarbon fraction on oxidation by permanganate yields a minute quantity of a substance, $C_9H_{14}O$, which may be tetrahydro-*p*-tolyl methyl ketone (VIII). The substances $C_{10}H_{16}O_2$ and $C_9H_{14}O$ are not obtainable by the separate oxidation of any of the known components (*p*-cymene, α-terpinene, *l*-limonene; see below) of the total hydrocarbon fraction, and it is consequently assumed that they come from the terpene * yielding the tetrabromide.

The same formula has been used already for Tschugaeff's *iso*-limonene (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 988) and Aschan's diprene (*Annalen*, 1924, **439**, 221), neither of which has been fully described, and it is possible that further work may prove all three to be identical, in which case the name *iso*limonene should have priority. It is of interest to note that all three occur along with limonene.

The removal of the readily oxidisable components (α-terpinene and terpene *A*) by partial oxidation of the total hydrocarbon fraction with chromic acid leaves a mixture of *p*-cymene and the lævorotatory component, the identity of which has been a subject of conjecture since 1907. On bromination followed by removal of the *p*-cymene, which inhibits crystallisation, *l*-limonene tetrabromide was isolated in good yield and the presence of *l*-limonene was confirmed by the formation of its characteristic oxidation products, hydroxyterpenylic and lævulic acids. It is also shown that on oxidation by permanganate in acetone, *l*-limonene yields an oily lactone acid, $C_9H_{14}O_5$, derived from a dihydroxy-dicarboxylic acid, $C_9H_{16}O_6$, for which the constitution

$$OH \cdot CHMe \cdot CH_2 \cdot CH_2 \cdot \overset{*}{C}H[CH(OH) \cdot CO_2H] \cdot CH_2 \cdot CO_2H$$

is suggested, since it furnishes lævulic and acetic acids by oxidation with chromic acid, fission taking place at $\overset{*}{C}$. This acid is closely related to two acids,

$$CH_2Ac \cdot CH_2 \cdot CHAc \cdot CH_2 \cdot CO_2H \longrightarrow$$
$$CO_2H \cdot CH_2 \cdot CH_2 \cdot CH(CO_2H) \cdot CH_2 \cdot CO_2H,$$

mentioned, without description, by Tiemann and Semmler (*Ber.*, 1895, **28**, 2150) as resulting from the oxidation of limonene erythritol.

In the course of this work large quantities of the total hydrocarbon fraction of chenopodium oil have been worked up, and from the first runnings of these a few c.c. of a substance, which is probably *sym*-dimethylethylene oxide, C_4H_8O, was isolated.

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* To save space, and to avoid further additions to the synonymy of terpenes, this component is referred to later as terpene *A*.

The following substances have now been identified as components of chenopodium oil.

p-Cymene.	*sym*-Dimethylethylene oxide (?).	Ascaridole.
a-Terpinene.	Butyric acid.	Ascaridole glycol.
$\Delta^{2:8(9)}p$-Menthadiene.	Methyl salicylate.	Ascaridole glycol
l-Limonene.	Salicylic acid.	anhydride.

The chief interest of chenopodium oil lies in its use as an anthelmintic, and it is being employed on a large scale in anti-hookworm campaigns in various parts of the world. Drs. Smillie and Pessôa, who have been engaged in researches on hookworm disease under the auspices of the Brazilian Government and the Rockefeller Foundation in Brazil, have kindly tested pharmacologically and clinically the chief components of chenopodium oil isolated in these laboratories, and their results have been published elsewhere (*J. Pharm. Expt. Ther.*, 1924, **24**, 359). They show that ascaridole, the chief component of the oil, is a remarkably efficient anthelmintic, and that none of the other constituents can be regarded as of value for this purpose.

EXPERIMENTAL.

When a receiver cooled in ice and salt was inserted during the separation of the hydrocarbon fraction from ascaridole by distillation at low pressure, a small amount of a colourless, volatile, pungent-smelling liquid was collected. On redistilling this, a little was obtained at 65—75°/760 mm., the greater part boiling between 120—170°, and consisting chiefly of terpenes and *p*-cymene. After drying over potassium carbonate, the lower-boiling fraction had b. p. 64—78°, $d_{15^\circ}^{15^\circ}$ 0·837, $d_{0^\circ}^{0^\circ}$ 0·8409, $[\alpha]_D^{15^\circ} + 0·10°$, $n_D^{20^\circ}$ 1·3968 to 1·3981, M (vapour density) 70·2 (Found : C, 66·4; H, 12·4. C_4H_8O requires C, 66·7; H, 11·1% ; M, 72).

The odour and the characters of this substance indicate that it might be one of the butylene oxides (possibly *sym*-dimethylethylene oxide), b. p. 56—57 ; $d_{0^\circ}^{0^\circ}$ 0·8344, but, as the figures given above show, the small quantity obtained was still highly impure.

The hydrocarbon fraction distilled between 170° and 185°/760 mm. but all attempts to isolate fractions of constant boiling point failed ; considerable separation was, however, effected by repeated slow distillation through a 12-bulb Young dephlegmator. Four litres of the hydrocarbon fraction so treated gave the following results :

Fraction	1	2	3	4	5
B. p.	170—174°	174°	174—175°	175—175·5°	175·5—176°
Amount (g.)	20	40	150	1100	30
a (1-dcm.) ...	−14°	−15°	−16°	−17°	−17·5°

Fraction	6	7	8	9
B. p.	176—177°	177—178°	178—180°	180—184°
Amount (g.)	800	800	900	150
a (1-dcm.) ...	−18°	−19°	−20°	−18·5°

α-Terpinene nitrosite could be obtained from all these fractions, while only fractions 1 to 4 gave the tetrabromide, m. p. 117°, characteristic of terpene A, the best yield being obtained from fraction 1. Fraction 4 was repeatedly redistilled to furnish a little more of fractions 1 to 3, and the residue used with fractions 6, 7, and 8 for the identification of the lævorotatory component. It was shown previously (*loc. cit.*, 1717) that the α-terpinene present in these fractions could be removed by agitation with Beckmann's chromic acid mixture, leaving the lævorotatory terpene mixed with *p*-cymene, and this mixture is referred to later as fraction B. It has the following average characters : b. p. 176·5° to 177°/758 mm., $d_{23°}^{23°}$ 0·8545, $[\alpha]_D^{15°}$ — 23·08°, $n_D^{20°}$ 1·48637 [Found : C, 89·1, 88·9, 88·8; H, 10·9, 10·6, 10·65%, which corresponds with a mixture of terpenes $C_{10}H_{16}$ (C, 88·2; H, 11·8) and *p*-cymene $C_{10}H_{14}$ (C, 89·6; H, 10·4) in proportion 40 : 60, and 63% of *p*-cymene can be isolated from it by oxidation with permanganate in acetone (see below)]. It yields no terpinene nitrosite, nor any of the oxidation products of α-terpinene, and no terpene A tetrabromide could be obtained from it.

Examination of Fraction B.

Bromination.—On bromination by the method already described (*loc. cit.*, p. 1717) a yellow, viscous oil was obtained which, even after standing for several months below 0°, deposited no crystals and gradually changed to a nearly solid tar. If, however, the freshly-brominated product, freed from chloroform and hydrogen bromide by aspiration, was quickly distilled until the bulk of the *p*-cymene was removed at about 105°/10 mm., the residual brown oil, on standing, became filled with leafy crystals, m. p. 104° after recrystallisation from alcohol. A mixture with an equal quantity of *d*-limonene tetrabromide melted at 124° and showed no depression of melting point on further admixture with dipentene tetrabromide. A mixture with the tetrabromide of terpene A (m. p. 117°) melted at 90—92°. The substance is therefore *l*-limonene tetrabromide (Found : Br, 69·9; $[\alpha]_D^{16°}$ — 66·12°. *l*-Limonene tetrabromide, $C_{10}H_{16}Br_4$, requires Br, 70·2% and has $[\alpha]_D^{9°}$ — 73·45°).

Oxidation by Permanganate in Acetone.—Fraction B (700 c.c.) mixed with acetone was treated with powdered potassium permanganate (1200 g.) in quantities of 10 g. at a time. The acetone was then distilled off and the residue steam-distilled, yielding 436 c.c. of *p*-cymene (62·3% of the mixture used) having α — 0·7°. The residual alkaline liquor, combined with the washings of the precipitated manganese dioxide, was concentrated to low bulk (compare *loc. cit.*, p. 1719), shaken with ether and ethyl acetate

to remove a small amount of neutral matter, from which traces of the carbonyl compound $C_9H_{14}O$ were isolated (p. 1658), then acidified and again extracted with ether (i), and ethyl acetate (ii). After removal of acetic acid by heating under reduced pressure, these extracts amounted to (i) 61·3 g. and (ii) 15·6 g. and consisted of oily acids, which could not be induced to crystallise either as such or in the form of derivatives. They were therefore converted into ethyl esters, and these distilled under reduced pressure, giving fraction (a), b. p. 117—170°/11 mm., $[\alpha]_D^{20°} - 4\cdot8°$; fraction (b), b. p. 170—215°/11 mm., $[\alpha]_D^{20°} - 4\cdot8°$, which from the long range of boiling point were obviously mixtures.

After many attempts to isolate a pure acid from these esters it was found that by hydrolysing them with sodium hydroxide in alcohol, a sodium salt, insoluble in alcohol, was produced, which though hygroscopic could be obtained in a granular condition by filtering rapidly from the excess of alcoholic soda, washing thoroughly with 96% alcohol, and drying in a vacuous desiccator. More of this sodium salt was secured by distilling the solvent from the mother-liquors and boiling the residue with dry alcohol. Finally, the viscous residual mixture of soluble sodium salts was dissolved in water, shaken with ether to remove a small amount of neutral tar that had formed, then acidified, and the liberated acid recovered by extraction with ether. This solvent having been distilled off, the acid was boiled with baryta, the excess of the latter removed by carbon dioxide, the filtrate taken to dryness in a vacuum, and the residue boiled with alcohol, which caused the separation of an insoluble barium salt, a little more of which was obtained by repeating the process. Finally, there was left a comparatively small amount of a mixture of barium salts soluble in alcohol, from which a little more material could be separated by precipitation as the thorium salt, but this method was not pursued further. The insoluble sodium and barium salts, isolated as described above, were purified as far as possible by repeated boiling with 96% alcohol, and then gave the following results on analysis, which showed them to be salts of the same acid. *Sodium* salt. Found : Na, 17·0%. *Barium* salt, Found : Ba, 39·1%. Calc. for $C_9H_{14}O_6Na_2$, Na, 17·4%; calc. for $C_9H_{14}O_6Ba$, Ba, 38·6%. The free acid, regenerated from either the sodium or barium salt, boiled at about 210°/34 mm. and formed a colourless, viscid oil (Found : C, 54·0, 53·9; H, 6·4, 6·8. $C_9H_{14}O_5$ requires C, 53·5; H, 6·9%).

On direct titration with N-soda solution no definite end-point could be obtained, but when the acid was boiled with excess of N-soda for at least 30 minutes and the excess of alkali titrated

back with N-acid satisfactory end-points were reached and the amount of soda used was equivalent on the average to sodium (Na) 22·19%. For conversion of $C_9H_{14}O_5$ into $C_9H_{14}O_6Na_2$ the amount of sodium (Na) required is 22·7%.

The silver salt of the acid is relatively stable at atmospheric temperatures even on exposure to light; it dissolves in boiling water and if the solution is filtered rapidly from the small amount of reduced silver formed, re-deposits the salt on cooling as a colourless granular powder, which, however, cannot be dried for analysis without the application of heat, which leads to reduction; and the results are always from 2 to 4% high in silver. Small amounts of the barium salt have been obtained in crystalline form by the cautious addition of alcohol to a 25% solution of the salt in water, but the crystals are very deliquescent, and it was not found practicable to secure enough crystallised barium salt for examination in this way.

The acid gave no derivative with semicarbazide, hydroxylamine, or phenylhydrazine.

To a solution of 2·6 g. of the sodium salt in 30 c.c. of water 30 c.c. of Beckmann's chromic acid mixture were added and the mixture was left standing with occasional agitation for 4 days. It was then thoroughly extracted with ether, which removed 1·52 g. of oily acids, smelling strongly of acetic acid. This residue was left in a vacuum over caustic potash until the bulk of the acetic acid was removed, and then treated with solution of semicarbazide in alcohol, when in the course of a few hours it deposited a copious crop of crystals of a semicarbazone, m. p. 182°; after recrystallisation from alcohol, this rose to 194° (corr.) and showed no change on further crystallisation and no depression when mixed with lævulic acid semicarbazone. The oxidation products of the $C_9H_{14}O_5$ acid are therefore lævulic and acetic acids, and in view of this and the results recorded above the authors regard this acid as a lactone of the acid OH·CHMe·CH$_2$·CH$_2$·CH[CH(OH)·CO$_2$H]·CH$_2$·CO$_2$H (p. 1650).

The acids regenerated from the barium salts soluble in alcohol referred to above also yield lævulic and acetic acids on oxidation with chromic acid and therefore probably still contain some of the $C_9H_{14}O_5$ lactone acid, which seems to be the principal product of the oxidation of limonene by permanganate in acetone solution.

Oxidation by Permanganate in Water.—Fraction B (100 c.c.) was added in four portions to 1 litre of water containing 94 g. of potassium permanganate, and shaken occasionally till decolorised. The mixture was then steam-distilled to remove unchanged hydrocarbon, and the residual liquor in the distillation flask, with the washings from the precipitated manganese dioxide, thoroughly

extracted with ether, yielding a little cuminaldehyde (derived from p-cymene), which was identified by a mixed melting point determination of the semicarbazone (m. p. 210°). The liquor was then concentrated to low bulk, made acid, and shaken with (i) ether and (ii) ethyl acetate. The ethereal extract after removal of the solvent was distilled under reduced pressure, and yielded two fractions, the first a thick oil and the second crystalline, m. p. 159—160°, and consisting of isopropenylbenzoic acid, formed by distillation of hydroxyisopropylbenzoic acid, which is known as an oxidation product of p-cymene under these conditions (Found : C, 73·6 ; H, 6·4. Calc. for $C_{10}H_{10}O_2$: C, 74·1 ; H, 6·2%. Found in silver salt : Ag, 40·9. Calc. for $C_{10}H_9O_2Ag$: Ag, 40·15%). The oily fraction gave a semicarbazone, which after recrystallisation melted constantly at 194° and showed no depression of melting point when mixed with lævulic acid semicarbazone (Found : C, 41·9 ; H, 6·7. Calc. for $C_6H_{11}O_3N_3$: C, 41·6 ; H, 6·3%). The ethyl acetate extract, on removal of the solvent, deposited a crystalline acid, m. p. 195° (Found : C, 50·2 ; H, 6·4. $C_8H_{12}O_5$ requires C, 50·85 ; H, 6·4%). The substance remained unchanged in m. p. after recrystallisation from boiling alcohol and produced no depression when mixed with hydroxyterpenylic acid, $C_8H_{12}O_5$, already known as an oxidation product of d-limonene (Godlewski, *J. Russ. Chem. Soc.*, 1899, **31**, 211).

As lævulic acid has not been previously mentioned as formed in the oxidation of limonene by permanganate in water, commercial limonene was oxidised as described above, and yielded hydroxy-terpenylic and lævulic acids, but no cuminaldehyde or isopropenyl-benzoic acid.

From the foregoing results it is clear that fraction B of the chenopodium oil hydrocarbons contains, in addition to p-cymene, l-limonene.

Nature of Terpene A.

As already stated, it has not been possible to isolate this terpene, or to obtain mixtures containing more than 10 to 12% of it as indicated by the amount of tetrabromide obtainable. For evidence of its constitution reliance has therefore had to be placed on (i) reactions of the only crystalline derivative, the tetrabromide, and (ii) the formation of certain substances when mixtures containing it are oxidised.

Oxidation of the Total Hydrocarbon Fraction by Chromic Acid.— The total hydrocarbon fraction of chenopodium oil was oxidised as already described (*loc. cit.*, p. 1717). After separation by steam distillation of the unattacked hydrocarbons (2150 c.c. from 2500 c.c.) there remained in the distillation flask 70 g. (about 1·5%) of a thick

oil, which, after drying, was distilled under reduced pressure, yielding an oil, b. p. 138—154°/19 mm., and a hard, pitch-like residue, which decomposed on further heating. The oil, after standing in solution in ether over potassium carbonate, was re-distilled in two fractions, b. p. 110—120°/15 mm. and 120—136°/15 mm. Both were pale yellow, viscous oils having a faint carvone-like odour; they yielded no solid derivatives with phenyl-carbimide or p-nitrobenzoyl chloride, but on addition of semi-carbazide in aqueous acetic acid solution were converted in the course of 3 days into semi-solid masses, which, when rubbed with alcohol, became crystalline, m. p. 140° (air-dry) and 194° when completely dried at 100°; after recrystallisation from boiling alcohol, they melted at 157° (air-dry) or 204° (dried at 120° in a vacuum), and these melting points were unchanged after a further crystal-lisation from alcohol. The acetic acid of crystallisation (see below) persists when the air-dry substance is crystallised from boiling alcohol, but if the dried substance is recrystallised from alcohol or boiling water the product obtained melts at 204° and is anhydrous. From all solvents the substance forms rosettes of transparent prisms [Found : loss on drying at 120° in a vacuum, 21·2%. $C_{11}H_{19}O_2N_3,C_2H_4O_2$ requires loss· (acetic acid), 21·05%. Found in dried material : C, 58·6, 58·7; H, 8·6, 8·4; N, 19·2. $C_{11}H_{19}O_2N_3$ requires C, 58·6; H, 8·5; N, 18·6%]. The substance is therefore a *semicarbazone* of a product, $C_{10}H_{16}O_2$, probably a *keto-alcohol*. When the semicarbazone is formed in presence of alcohol and acetic acid, or when it is repeatedly boiled with water, there is formed a *base* which has only been isolated as the *acetate*, minute rosettes of needles, m. p. 206°, from water by slow evaporation, and the *picrate*, brilliant yellow needles, m. p. 158°, from acetone or acetone and benzene. This differs from the semicarbazone by the elements of a molecule of water [Found (i) in acetate : C, 57·5, 58·2; H, 8·3, 8·1. $C_{11}H_{17}ON_3,C_2H_4O_2$ requires C, 58·05; H, 7·8%. Found (ii) in picrate : N, 18·6. $C_{11}H_{17}ON_3,C_6H_2(NO_2)_3 \cdot OH$ requires N, 19·3%].

It is clear from this that the semicarbazone readily undergoes internal condensation, losing a molecule of water, and on this account it is regarded as having the constitution represented by formula (VI), and the base $C_{11}H_{17}ON_3$ formed from it as having formula (VII).

Only part of the oil reacts with semicarbazide solution and after the whole of the semicarbazone has been separated the mother-liquor on dilution with water yields a thick oil, which can be extracted with ether. This could not be induced to crystallise, nor could it be distilled without some decomposition. It appears,

however, to be a derivative of α-terpinene, since on oxidation with aqueous permanganate it gave a good yield of the mixed *anti*- and *para*-forms of αδ-dihydroxy-α-methyl-δ-*iso*propyladipic acid, m. p. 189°, and showed no depression of melting point on addition of a recrystallised mixture in equal parts of these two forms of this acid (J., 1923, **123**, 1878).

In this oxidation by Beckmann's mixture, α-terpinene is converted into dimethylacetonylacetone, the yield being about 3% of the total hydrocarbon fraction taken. The substance was identified by conversion into the semicarbazide derivative, which melted at 201° and showed no depression of melting point when mixed with the semicarbazide derivative prepared from synthetic dimethyl-acetonylacetone (Found : C, 59·2 ; H, 8·9 ; N, 23·05. Calc. for $C_9H_{15}ON_3$: C, 59·7 ; H, 8·3 ; N, 23·2%). Some *p*-tolyl methyl ketone was also formed in the oxidation, and was identified by means of its semicarbazone (Found : C, 62·1 ; H, 6·6. Calc., C, 62·8 ; H, 6·8%), m. p. 210°, which showed no depression when the substance was mixed with *p*-tolyl methyl ketone semicarbazone. α-Terpinene, *d*-limonene, and *p*-cymene have all been treated separately with Beckmann's mixture, and their oxidation products are being examined, but none of them yields the substance $C_{10}H_{16}O_2$ described above, and it seems safe to assume that this is derived from terpene *A*.

Oxidation of the Total Hydrocarbon Fraction by Permanganate in Acetone.—When the total hydrocarbon fraction is oxidised by permanganate in acetone, the principal products are a mixture of the *para*- and *anti*-forms of αδ-dihydroxy-α-methyl-δ-*iso*propyl-adipic acids already described by the authors (J., 1923, **123**, 1878) and dimethylacetonylacetone, resulting from the further oxidation of these acids derived from α-terpinene, *p*-tolyl methyl ketone, and a little cuminic acid, both arising from *p*-cymene, and a mixture of optically active oily acids identical with those, described above (p. 1653), derived from *l*-limonene. The only other product was obtained by extracting the concentrated neutral aqueous liquors with ether, which removed a viscous, brown oil too small in amount to permit of direct purification. From this a crystalline semicarbazone was obtained, which on recrystallisation from boiling alcohol formed colourless needles, m. p. 204° (corr.), which became yellow on exposure to light (Found : C, 61·3, 61·5 ; H, 8·7, 8·15 ; N, 21·3. $C_{10}H_{17}ON_3$ requires C, 61·5 ; H, 8·7 ; N, 21·5%). On hydrolysis, the semicarbazone furnishes an oil smelling like a mixture of menthone and cuminaldehyde, and from this oil the semicarbazone cannot be regenerated. This semicarbazone is optically inactive, and, if it comes from terpene *A*, should be

that of Δ^2-tetrahydro-p-tolyl methyl ketone, $C_9H_{14}O$ (VIII), but as the yield of semicarbazone obtained only amounts to 0·24% of the total hydrocarbon fraction used, it has not been possible to accumulate enough for examination in detail.

Tetrabromide of Terpene A.—The preparation and isolation of the tetrabromide has been described already (*loc. cit.*, p. 1717). Of numerous attempts to use this tetrabromide as a means of gaining information regarding the constitution of terpene A, only the following have given useful results. 12·5 G. of the tetrabromide were added to a solution of 1·9 g. of sodium in methyl alcohol, and the mixture, after boiling for 7 hours, was steam-distilled, when 4·4 g. of a heavy, colourless oil were obtained, b. p. 115—120°/18 mm., containing 30·2% of bromine ($C_{10}H_{14}Br \cdot OMe$ requires Br, 32·6%). This appeared to be a monobromomethyl ether corresponding to the monobromomethyl ether which Wallach obtained from limonene tetrabromide (*Annalen*, 1894, **281**, 127). The removal of the fourth bromine atom by the further use of sodium converted the monobromomethyl ether almost wholly into p-cymene. Unlike Wallach's product, it did not after reduction yield a menthenone by oxidation with either chromic acid or permanganate. It was only slowly attacked by either agent, and the products in both cases were p-tolyl methyl ketone with a little p-toluic acid. In further experiments, silver acetate was used : 5·3 g. of the tetrabromide were shaken with 5·8 g. of silver acetate in 10 c.c. of acetic acid during 8 hours, then made alkaline with sodium carbonate, and shaken with ether, which removed a yellow, viscous oil (3·1 g.). This on solution in light petroleum (b. p. 40—60°) deposited some insoluble tar, and the oil thus purified, after drying over potassium carbonate and removal of the petroleum by distillation and exposure in a vacuum until of constant weight, gave the following results : C, 52·8 ; H, 6·1 ; Br, 29·2 ($C_{10}H_{14}Br \cdot O \cdot CO \cdot CH_3$ requires C, 52·6 ; H, 6·2 ; Br, 29·3%). The substance is therefore a *bromoacetoxydihydro*-p-*cymene* (II) and this was confirmed by hydrolysing a weighed quantity (0·2175 g.) of the substance in the cold with a known amount of potassium hydroxide in alcohol (30·6 c.c. of $N/10$-KHO), the mixture being allowed to stand for a week, after which the excess of alkali (16·42 c.c. of $N/10$-KHO) was determined by titration with standard nitric acid. The amount of alkali used (14·2 c.c of $N/10$-KHO), after correction for a small amount of bromide (equal to 0·0478 g. Br) formed, was 21·1%, whilst that required for the removal of one acetyl group from $C_{10}H_{14}Br \cdot O \cdot CO \cdot CH_3$ is 20·5%.

Seven g. of the bromoacetoxy-compound were agitated with 30 c.c. of water to form an emulsion ; to this 130 c.c. of Beckmann's

chromic acid mixture were added in three portions at intervals of 1 hour, and the whole was shaken for 8 hours. This was extracted with (1) light petroleum, b. p. 40—60°, and (2) ether, and the extracts were dried over anhydrous sodium sulphate. The petroleum extract (1) left an oily residue (2·9 g.) which was pungent, and had an odour of p-tolyl methyl ketone; on treatment with semicarbazide it yielded a semicarbazone which after crystallising twice from boiling alcohol formed colourless, opaque prisms melting constantly at 210° and showing a slight rise in melting point to 211° when mixed with an equal quantity of p-tolyl methyl ketone semicarbazone prepared from synthetic material. The mother-liquor from the preparation of the semicarbazone was made alkaline with sodium carbonate and shaken with light petroleum, when it yielded 1·7 g. of an oil containing bromine and apparently consisting largely of unchanged material. The ether extract (2) yielded on re-extraction with sodium carbonate solution and acidification of this (a) terephthalic acid, colourless crystals, subliming without melting above 280°, and (b) p-toluic acid, m. p. 177°, showing no depression when mixed with a pure specimen of p-toluic acid.